

Low compressible noble metal carbides with rock-salt structure: *ab initio* total energy calculations of the elastic stability

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We have systematically studied the mechanical stability of all noble metal carbides with the rock-salt structure by calculating their elastic constants within the density function theory scheme. It was found that only four carbides (RuC, PdC, AgC and PtC) are mechanically stable. In particular, we have shown that RuC, PdC, and PtC have very high bulk modulus, which has been remarkably observed by the most recent experiment for the case of PtC. From the calculated density of states, we can conclude that these compounds are metallic, like the conventional group IV and group V transition metal carbides.

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Transition metal carbides (TMCs) have attracted much attention due to their excellent physical, chemical and mechanical properties.[1, 2] In the past, most work was focused on the group IV and group V TMCs,[3, 4, 5, 6, 7] while noble metal carbides have been only studied spectroscopically by few researchers[8, 9, 10] because the crystalline samples are hard to obtain. Very recently, shortly after the synthesis of a novel noble-metal nitride, PtN,[11] Shigeaki Ono *et al.*[12] have succeeded for the first time in synthesizing platinum carbide (PtC) at high-pressure and high-temperature by the laser-heated diamond anvil cell technique. According to their report, the new PtC has a rock-salt (RS) structure, with a high bulk modulus of 301 (± 15) GPa.

While the structural and electronic properties of earlier-synthesized PtN have been extensively studied in recent theoretical[13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23] and experimental[24] work, very few attention has been paid to the PtC system. Recently, Li *et al.*[25] have given a first-principles calculation of PtC. They preferred PtC crystallized in zinc-blende (ZB) structure since their results showed that the RS-PtC is mechanically unstable. In contrast, after a systematic calculation, and based on two separate DFT schemes, we found that the RS-PtC is mechanically stable[26] and the compressibility behavior of RS-PtC is more comparable with that of the experiment. To illustrate, here we show in Fig. 1 the calculated pressure-volume relation for both ZB- and RS-PtC. For comparison, the experimental data[12] are also plotted. Clearly, one can see that the calculated com-

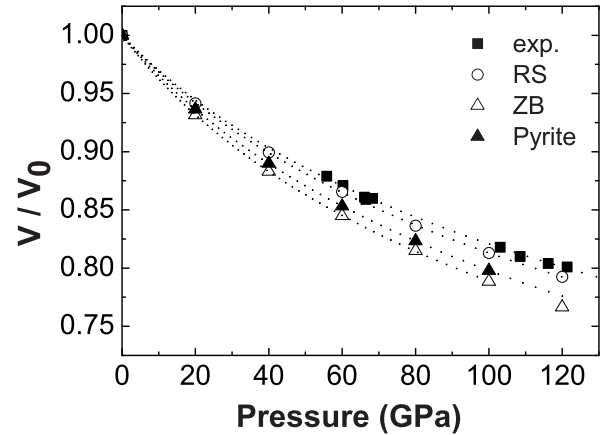


FIG. 1: Calculated Pressure-Volume data (average LDA and GGA results) of PtC with RS and ZB structure, PtC₂ with Pyrite structure and experimental data. Dashed curves are the third-order Birch-Murnaghan equation fit with $B=289$ (239, 257, 301) GPa and $B'=5.0$ (4.7, 4.6 5.3) for the RS (ZB, Pyrite, exp.).

pressibility ratio for RS-structure is in good agreement with the experimental result while it is not so for ZB-structure. Therefore, our results firmly show that the observed phase of PtC under high-pressure is rocksalt, although it is difficult to distinguish the structures of RS from ZB only by X-ray diffraction measurement[27]. We have also found[26] that the total energy of the ZB structure is lower than that of the RS structure (about

1 eV/unit cell). From this sense, the synthesized PtC in Ref.[12] is metastable. In addition, we have further calculated the elastic constants of PtC₂ with the fluorite and pyrite structures, since the former structure was once proposed to explain the high bulk modulus of platinum nitride and the latter structure has been recently observed[24] in platinum nitride. Our calculation revealed that the fluorite PtC₂ is mechanically unstable. On the other hand, the pyrite PtC₂ is calculated to be mechanically stable but with a low bulk modulus ($B=236$ GPa, $B'=4.7$), much lower than that of the experiment.[12] What's more, there also exists a big discrepancy between the calculated pressure-volume data of pyrite PtC₂ and those of experiments (see Fig.1). Therefore, we excluded the possibility of existence of zincblende or pyrite structure in the experiment.[12]

To appreciate the consistency of our calculation with the experimental observation on PtC and its very high bulk modulus, in this paper we have gone beyond to search in a systematic way for other possible mechanically stable noble-metal carbides with the RS structure by calculating the relevant elastic constants. Surprisingly, we have found that RuC has even higher bulk modulus of ~ 370 GPa. Among the whole noble metal (Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au), Ag and Pd were also found to form mechanically stable carbides. Together with RuC and PtC, they form a new family of low compressible compounds. The partial density of states (PDOS) of RuC, PdC, AgC, and PtC were calculated, which revealed that the hybridization of metal $5d$ -like and C $2p$ -like states is responsible for the strong covalent bonding of these compounds. The PDOS also revealed that these compounds are of metallic character.

The first-principles calculations were performed by the plane-wave pseudo-potential (PW-PP) method as implemented by CASTEP code[28]. The ultrasoft pseudopotential (USPP)[29] was used to describe the interaction between ions and electrons. The exchange and correlation terms were described by the local-density approximation (LDA)[30] and generalized gradient approximation (GGA)[31]. For the Brillouin-zone sampling, the Monkhorst-Pack (MP) scheme[32] with a mesh of (12, 12, 12) was adopted. We chose $E_{\text{cut}}=550$ eV for all the calculations. It was tested that with even more strict parameters the total energy can be converged within 0.003 eV/atom for all the cared systems. For the mechanical stable phases, the elastic constants were recalculated with the full-potential linearized augmented plane-wave (LAPW) method[33] (implemented by WIEN2K), wherein a non-overlapping muffin-tin (MT) sphere radius of 2.2 (2.1, 2.3, 2.3) a.u. for Ru (Pd, Ag, Pt) and 1.7 (1.5, 1.7, 1.7) a.u. for C atoms in RuC (PdC, AgC, PtC) compound was employed. The valence wave functions inside the MT spheres were expanded into spherical harmonics up to $l=10$ and the potential up to $l=4$ for the $4d$ carbides and $l=6$ for the $5d$ carbide (PtC). The energy that sepa-

rates the core and valence states was set to be $-6.0 R_y$ for the $4d$ carbides and $-7.0 R_y$ for the $5d$ carbides. Here, an APW+lo[34] type basis set for certain electronic states was also used. We used 5000 k points for sampling the Brillouin zone and $R_{\text{mt}} \times K_{\text{max}}$ was taken as 8.0 (where R_{mt} is the muffin-tin radius and K_{max} is the plane-wave cutoff). A fully relativistic calculation was performed for core states, whereas the valence states were treated in a scalar relativistic scheme.

After getting the equilibrium geometry configures, in the PW-PP method we applied the so-called “stress-strain” method to obtain the elastic constants. For the cubic crystal, there are only three different symmetry elements (c_{11} , c_{12} and c_{44}). A single strain with non-zero first and fourth components (xx and yz) can give stresses relating to all three of these coefficients, yielding a very efficient method for obtaining elastic constants for the cubic system. The elastic constants can be obtained from the stress-strain relations and then the bulk modulus is obtained from the elastic constants by equation $B=(c_{11}+2c_{12})/3$. In the LAPW method another scheme was adopted (For details read document in WIEN2K package). In this scheme, three types of deformation were performed to produce three linear equations for c_{11} , c_{12} , and c_{44} .

Table I lists the calculated elastic properties of the mechanically stable noble metal carbides. One can see that the results from the PW-PP method and those from the LAPW method fit very well. An exception is the amplitude of c_{44} in PtC and RuC; the inconsistency between the two methods remains unclear. However, since the amplitude of c_{44} does not affect the value of the bulk modulus of these compounds, we do not care about it at present. As it is well known that in first-principles calculations the LDA (GGA) usually underestimates (overestimates) the lattice constant and overestimates (underestimates) the bulk modulus, hence we adopt in the PW-PP method to use the average of LDA and GGA values as the re-scaled estimates. The responses of the crystal under hydrostatic pressure, rhombohedral, and tetragonal distortions are measured by the bulk modulus B , the normal shear modulus $G' = c_{44}$, and the tetragonal shear modulus $G'' = (c_{11}-c_{12})/2$, respectively. The mechanical stability of a crystal requires the strain energy to be positive, which for cubic crystal implies[35]

$$c_{44} > 0, c_{11} > |c_{12}|, c_{11} + 2c_{12} > 0. \quad (1)$$

From Table I we can see that the listed four carbides are all stable because their elastic constants satisfy formula (1). One can find that among these compounds RuC has the highest bulk modulus with the value ~ 347 GPa, which is comparable with that of cubic BN (367 GPa[36]). The PtC has a theoretical bulk modulus of 288.7 GPa, in good agreement with the experimental value of 301 GPa. Thus Table I shows that the rocksalt RuC, PdC,

TABLE I: The calculated equilibrium lattice parameters $a(\text{\AA})$, elastic constants c_{ij} (GPa), bulk modulus B (GPa), tetragonal shear modulus G'' (GPa), polycrystalline shear modulus $G=(c_{11}-c_{12}+3c_{44})/5$ (GPa), Young's modulus E (GPa) and Poisson's ratio of four mechanically stable noble metal carbides.

		a	c_{11}	c_{44}	c_{12}	G''	B	G	E	ν
RuC	PW-LDA	4.236	604.9	0.9	252.8	176.1	370.2	71.0	200.2	0.41
	PW-GGA	4.299	504.5	8.8	233.8	135.4	324.0	59.4	168.0	0.41
	Ave.	4.268	554.7	4.9	243.3	155.8	347.1	65.2	184.1	0.41
	LAPW	4.327	487.7	21.6	226.7	130.5	313.7	65.2	182.9	0.40
PdC	PW-LDA	4.340	411.5	48.4	214.6	98.5	280.2	68.4	166.4	0.22
	PW-GGA	4.430	297.9	43.8	176.2	60.9	216.8	50.6	140.8	0.39
	Ave.	4.385	354.7	46.1	195.4	79.7	248.5	59.5	103.6	0.31
	LAPW	4.433	278.3	41.8	189.6	44.4	219.2	42.8	120.5	0.41
AgC	PW-LDA	4.543	246.0	17.6	147.7	49.2	180.4	30.2	85.8	0.42
	PW-GGA	4.665	185.3	14.3	113.0	36.2	137.0	23.1	65.6	0.42
	Ave.	4.604	215.7	16.0	130.4	42.7	158.8	26.7	75.7	0.42
	LAPW	4.657	189.8	8.2	113.2	38.3	138.7	26.7	75.3	0.41
PtC	PW-LDA	4.425	373.6	47.0	284.0	44.8	313.9	46.1	131.8	0.43
	PW-GGA	4.506	277.8	51.7	256.4	10.7	263.5	35.3	101.4	0.44
	Ave.	4.466	325.7	49.4	270.2	27.8	288.7	40.7	116.6	0.44
	LAPW	4.489	272.8	11.9	255.5	8.7	261.3	10.6	31.4	0.48
Exp.(Ref.[12])		4.814					301 \pm 15			

together with PtC, form a new family of low compressible compounds.

We notice that the trends of bulk modulus in these carbides are in some way related to the number of valence electrons. This can be seen by the fact that the value of bulk modulus decreases with increasing the total number of valence electrons (12 per primitive cell for RuC, 14 for PdC and PtC, and 15 for AgC). To further investigate the origin of the bulk modulus, we have calculated the partial DOS of these carbides. The results are shown in Figs. 2. For RuC (Fig. 2a), there exists a minimum in DOS near the Fermi level, giving the value of about 0.6 states/eV per primitive cell. The states between -15 eV and -11 eV are mainly composed of C ($2s$) states with a little contribution from Ru ($4d$) states. There exist two peaks of the Ru ($4d$) states between -9 eV and the Fermi level. The strong hybridized states of Ru ($4d$) and C ($2p$) states between -9 eV and -4 eV is responsible for the covalent bonding of RuC. For PdC and PtC which contains two more valence electrons than RuC, the extra electron fills the anti-bonding d orbital of transition metal atoms, thereby decreasing the bonding strength of such compounds. As a consequence, the bulk modulus of PdC and PtC are much lower than that of RuC. The same rule can apply to AgC. One may ask the question why there is an invisible difference of bulk modulus between PdC and PtC. This can be explained as follows: the presence of $4f$ electrons in the latter compound, which should repel d -orbitals out of core regions thus enhance the d - p bonding (see the DOS patterns of

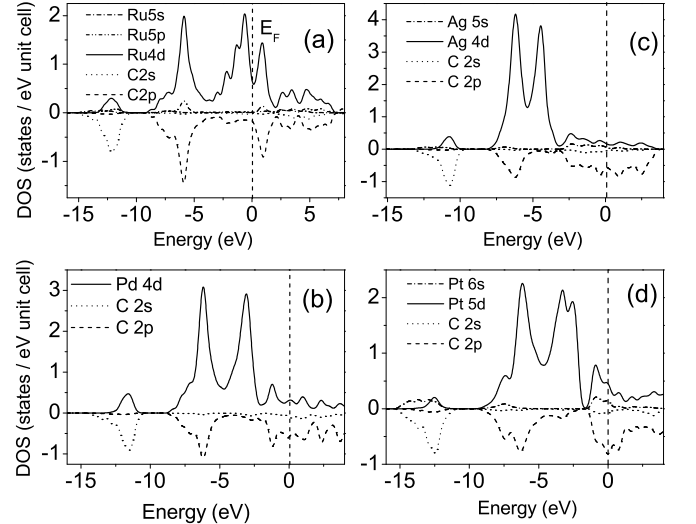


FIG. 2: Partial DOS of (a) RuC, (b) PdC, (c) AgC and (d) PtC with rock-salt structure.

Fig. 2b and Fig. 2c), giving a higher value of bulk modulus for PtC. In another way for a quantitative analysis, we have investigated the Fermi energy position of PtC, PdC and AgC compared to RuC, whose Fermi energy locates at d states of transition metal atoms. We find the more the Fermi level separated from d states, the lower the bulk modulus approaches. The trend is compatible with above proposed mechanism for bulk modulus de-

crease. Furthermore, from Figs. 2 one can conclude that all these four carbides are metallic.

As mentioned above, the tetragonal shear modulus G'' measures the response of a crystal to the volume-conserving tetragonal shear strain. It is thought that the stretching of metal-C bonds and the bending of metal-metal bonds are involved in such procedure[37]. Because c_{11} is determined by the nearest-neighbor interaction as well as bulk modulus B , thus when $c_{11} \gg c_{12}$, G'' have the same trend as B , as we observed in RuC and PdC in Table I. However, when c_{11} is comparable to c_{12} , the shear modulus trend does not need to be similar as that of bulk modulus. For example, in the present calculations, the bulk modulus of PtC is 288.7, much larger than that of AgC (158.8 GPa). However, its G'' (27.8 GPa) is smaller than that of AgC (42.7 GPa).

The nature of hardness has been extensively investigated and many new models have been proposed[38, 39, 40, 41, 42]. Although for the strong covalent materials, the hardness can be directly evaluated[41, 42], for the partially covalent transition-metal based hard materials, the polycrystalline shear modulus $G [(c_{11} - c_{12} + 3c_{44})/5]$ is still considered as the most important parameter besides the bulk modulus, governing the indentation hardness. Our calculated polycrystalline shear modulus G of RuC is 65.2 GPa, which is the highest value of these four noble metal carbides. This value is just comparable to that of pure Pt (61 GPa[43]), remarkably contrasting the very high value of bulk modulus. It was also found that the highest shear modulus c_{44} of these four compounds (PtC: 49.4 GPa) is much lower than that of conventional materials. For example, the c_{44} of pure Pt is 76.4 GPa.[43] Therefore these four potential noble metal carbides are not expected to withstand shear strain to a large extent and may have very low hardness.

In conclusion, we have performed systematic *ab initio* total energy calculations on the elastic stability of all the rock-salt structured noble metal carbides. It was found that four carbides, namely RuC, PdC, AgC and PtC, are mechanically stable. Most of these potential transition metal carbides have low compressibility though their hardness is not expected to be high. The low compressibility was found to be related to the occupancy of the valence states. From the calculated electronic structure, all these carbides is metallic. Since the rock-salt PtC has been recently synthesized under high pressure and high temperature, we expect the other three carbides can also be prepared under certain extreme conditions.

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